DEVELOPMENT OF PROCESSING TECHNIQUES FOR ADVANCED THERMAL PROTECTION MATERIALS

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Introduction

Thermal Protection Materials Branch (TPMB) has been involved in various research programs to improve the properties and structural integrity of the existing aerospace high temperature materials. Specimens from various research programs were brought into the analytical laboratory for the purpose of obtaining and refining the material characterization. The analytical laboratory in TPMB has many different instruments which were utilized to determine the physical and chemical characteristics of materials. Some of the instruments that were utilized by the SJSU students are: Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), X-ray Diffraction Spectrometer (XRD), Fourier Transform-Infrared Spectroscopy (FTIR), Ultra Violet Spectroscopy/Visible Spectroscopy (UV/VIS), Particle Size Analyzer (PSA), and Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The above mentioned analytical instruments were utilized in the material characterization process of the specimens from research programs such as: aerogel ceramics (I) and (II), X-33 Blankets, ARC-Jet specimens, QUICFIX specimens and gas permeability of lightweight ceramic ablators. In addition to analytical instruments in the analytical laboratory at TPMB, there are several on-going experiments. One particular experiment allows the measurement of permeability of ceramic ablators. From these measurements, physical characteristics of the ceramic ablators can be derived.

Scanning Electron Microscopy & Energy Dispersive X-ray analysis

Scanning Electron Microscopy (SEM) is one of the major materials characterization techniques used routinely at TPMB. Materials characterization process of high-temperature aerospace materials is divided into two aspects. The two aspects are physical and chemical. The physical aspect deals with the corporeal characteristics of the material such as microstructure, relative grain size, grain growth, bonding pattern, and bonding structure. In order to determine the above mentioned physical aspect of a material, one needs to work with a materials characterization technique called SEM. In addition, the chemical aspect of

a material deals with the elemental make-up and chemical behavior of the materials. Chemical analysis include determination of elements and compounds present and also the chemical properties of a material. To determine the chemical aspect of a material, one needs to apply a technique called Energy Dispersive X-ray analysis (EDX).

Research Program: Aerogel Ceramics (I)

Aerogel ceramics (I) is a research program which dealt with seventeen specimens. Each of these specimen had a base form of either fibrous or crystalline structure. Most of these specimens were coated with either metal or silica aerogel coatings. The metal coatings used in this research program include gold (Au), chromium (Cr), gold and chromium (Au-Cr) , and IMI after heat treatment. After the coating process, a few specimens were subjected to various types of heat treatment; other specimens were not heat treated. Thus, the main intention of this research program was to determine whether the coating has migrated into the "base material" (fibrous or crystalline substrate) as a result of the heat treatment; if so how well the coating adheres to the substrate.

The main purpose of the SEM analysis was to characterize the following issues, and they are as follows: What happened to the coating materials? Did the coating materials migrated into the substrate? Is it possible to capture high resolution images? Is it possible to view how the flat crystals adhere to one another as a result of various chemical processes involved? Also, other purposes were to analyze the uncracked regions of the fibers so that the adherence capacity of the coating materials can be learned, and to characterize the change in the surface texture of each specimen as a result of various heat treatments involved. Therefore, SEM analysis was performed to obtain the above mentioned physical aspects of aerogel ceramics specimens.

During SEM analysis, many of these specimens experienced charging effect. As a result of the charging effect, the actual surface characteristics of each specimen was not available to capture in a photomicrograph. Thus, many of these specimens were sputtered

with gold-palladium (Au-Pd) coatings to minimize the charging effect. Energy Dispersive X-ray analysis technique was also applied in this research program to determine the chemical aspects. For example, EDX technique was applied to find out what new elements are accumulated on the specimen as a result of the heat treatment. EDX technique was also used to compare and contrast the percent element present at the interface between fiber/aerogel for various specimens; these specimens had approximately 0.5 mm thickness of silica aerogel coatings.

Research Program: Aerogel Ceramics (II)

Once again, specimens from another research program called aerogel ceramics (II) were analyzed via the SEM to obtain information such as how well the silica aerogel coating adheres to the ceramic substrates as a result of the different chemical treatments involved in bonding. In addition, specimens from aerogel ceramics (II) were also used to analyze the surface characterization, namely surface texture, because specimens from aerogel ceramics (II) were subjected to various types of chemical processes and heat treatments. Aerogel ceramics (II) research program consisted of two major types of ceramic blankets and they are Nextel and Fiberglass.

In this research program, Nextel and Fiberglass specimens were thought of as the base materials. These two base materials were subjected to ten different chemical processes. As a result, twenty specimens were generated with the silica aerogel coating of about 0.5 mm in thickness. The chemical processes applied in this research program were: Acid wash, Acid wash (diluted), Base wash, and No wash. Different types of chemistry used in this research program were: TMOS, TEOS, and Silbond.

The above mentioned twenty specimens, from the research program called aerogel ceramics (II), were analyzed with the aid of SEM. Once again, the analysis of SEM include how well or badly the silica aerogel coating adheres to the ceramic base materials as a result of the different chemical processes and the heat treatments. This research program

only dealt with the determination of the chemical aspect of aerogel ceramics (II) specimens.

Research Program: X-33 ceramics blankets

The purpose of this research program was to detect and quantify the amount of silicon carbide (SiC) particles present in the substrate material as a result of the coating. Once again, Energy Dispersive X-ray analysis (EDX) was utilized to identify the quantitative information such as what percent of carbon and silicon are present with in the specimen. Furthermore, SEM photomicrographs were also taken to illustrate the surface characterization of these specimen.

Research Program: ARC-JET specimens

ARC-JET specimens were brought into the TPMB analytical laboratory to capture the surface characterization of these specimens because these specimens were subjected to different coatings and heat treatments. Therefore, SEM analysis was used to obtain photomicrographs of various magnification. Thus, these photomicrographs showed how the coating layers embedded into the substrate material. Energy Dispersive X-ray analysis (EDX) was used to detect and to quantify the amount of chemical elements that are present in the substrate material.

X- Ray Diffraction Spectrometer

X-ray diffraction spectrometer analysis provided useful information in two areas. First, standard diffraction patterns were taken of each specimens prior to testing to check for impurities and unexpected phase transformation that may have been produced due in part to the processing steps. Second, the post test specimens were analyzed to detect the structure of the specimen. The structure of the specimen could either be crystalline or

amorphous. Thus, XRD analysis played an integral part in the detection process of the structure of the given specimen.

Research Program: QUICFIX specimens

Many quicfix specimens were brought into the TPMB laboratory because these specimens were used in various experiments to study the following information. For example, SEM analysis was performed to capture various high resolution images of these specimens. EDX analysis was conducted to learn about qualitative elemental analysis of these specimens. XRD analysis was also carried out to determine the structure of these specimens; the pre and post-test specimens were used in the process of the determination of the structure of various quicfix specimens.

Particle Sizer Analyzer

The laser light scattering is an exceptionally flexible sizing technique able in to measure the size of any one material phase in another. The only requirement of the technique is that each phase must be distinct optically from the other and the medium must be transparent to the laser wavelength. This means in practice that the refractive index of the material must be different from the medium in which it is supported.

This apparatus is used to measure a variety of different specimens in the analytical laboratory. It is important for defining certain physical characteristics of a specimen. The particle diameter that can be analyzed ranges from 0.1 μm to 600 μm with an error in the volume mean diameter of +/- 4 %. There is no sample preparation or calibration needed to utilize this instrument.

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES)

One method used to determine the chemical composition of a material is the ICP-AES. The ICP-AES is capable of quantitatively analyzing solutions for specified elements

with defining accuracy. When sample solutions are properly prepared and the ICP properly calibrated, an accuracy of less than one percent error is obtainable. Elements often determined are boron, silicon, aluminum, and zirconium in ceramic samples.

In order to prepare a sample the specimen must be put into a solution form. Most often, samples undergo dissolution with mineral acids in order to prepare them for analysis. However, there are samples that are very resistant to dissolving in a mineral acid. These samples contain high amounts of borides and carbides. In order to dissolve these compounds a alkali carbonate or nitrate flux followed by mineral acid treatment is required to be able to analyze these samples.

Research Program: High purity silica powder

High purity silica powder is a research program which dealt with two specimens. These specimens were used to mend cracks that occur on the ceramic tiles. In theory, the two specimens were to have the same chemical composition. The difference in the two specimens was seen when they were applied on the ceramic tiles to mend the cracks. One specimen mended the cracks but the other specimen did not.

The goal was to analyze the specimens to determine if there was any discrepancies in the elemental composition along with any trace contaminants. This was accomplished initially by converting the powdered specimen into a solution form. Finally, the specimens were quantitatively analyzed using the ICP-AES. In conclusion, it was found that one specimen consisted of a larger quantity of titanium than the other.

Permeability of Ceramic Ablators[3]

Many light weight thermal protection system (TPS) materials have a large degree of open porosity which can make them highly permeable to gas flow. In order to model internal gas flows in porous materials, knowledge of the gas permeability is required. Unfortunately this property is not readily available for most TPS materials. Recently, in

the TPMB, a permeability measurement apparatus was constructed to test rigid, porous TPS materials, and measurements were reported for a variety of TPS tile insulation's form the LI, FRCI, and AETB families, as well as for the commercial product FiberForm. This note presents further gas permeability measurements, made with the same apparatus, on a lightweight ceramic ablator (LCA) material called Phenolic Impregnated Carbon Ablator (PICA). LCA materials use tile insulation's as substrates which are partially impregnated with an organic resin to provide additional cooling mechanisms via endothermic decomposition's, pyrolysis gas heat transport, and boundary layer blowing. PICA material was developed at NASA Ames Research Center as lightweight ablative materials with enhanced structural integrity. PICA is actively used in TPS systems. PICA was selected as the forebody heat shield material for the Stardust capsule, is baselined for Genesis, and is under consideration for the Mars 2005 sample return capsule. Permeability data for LCA material is of particular importance since issues such as hot boundary-layer gas penetration and the detailed flow pattern of decomposition's (pyrolysis) products cannot be computationally evaluated until such data are measured.

Because the resins in PICA decompose at high temperature, the microstructures, and thus the permeability parameters Ko and b, of PICA samples are functions of their heating environment. This dependence includes the chemical composition the ambient gases, as well as the detailed heating history to which a sample is exposed. There are obviously a myriad of possible heating environments. In this work measurements are reported for the virgin LCA material and for material carred to its resin pyrolyisis endpoint in an inert atmosphere. These measurements of the permeability parameters Ko and b for virgin and charred specimens can be referenced in the attached appendix. The resin pyrolysis was accomplished by cycling specimens to about 1250 K in a tube furnace under an argon flow. Under these conditions, car yield of the phenolic resin in PICA is about 0.63.

Reference

[3] Jochen Marschall and Michael E. Cox "Gas permeability of the Lightweight Ceramic ablators PICA and SIRCA," January 1998; submitted to Journal of Thermophysics and Heat Transfer

Table 1. PICA data gathered for the contract period of June - December

Virgin						
Sample #	Orientation	Length(m)	Mass V (g)	ρ (lb/ft3)	Ko (m2)	b (Pa)
1	Transverse	0.01996	1.08	13.27	N/A	N/A
2	Transverse	0.01996	1.07	13.1	N/A	N/A
3	Transverse	0.01996	1.09	13.35	1.52E-11	3424
4	Transverse	0.01996	1.07	13.15	1.16E-11	4082
5	Transverse	0.01996	1.07	13.07	1.12E-11	4629
6	Transverse	0.02995	1.60	13.06	1.35E-11	3733
7	Transverse	0.02995	1.61	13.12	1.25E-11	3800
8	Transverse	0.02995	1.59	12.96	1.57E-11	3414
10	In-Plane	0.01996	1.10	13.55	4.05E-11	1628
11	In-Plane	0.01996	1.15	14.08	N/A	N/A
12	In-Plane	0.01996	1.15	14.09	3.49E-11	2092
13	In-Plane	0.01996	1.13	13.82	4.85E-11	1618
14	In-Plane	0.01996	1.14	13.96	N/A	N/A
15	In-Plane	0.02995	1.69	13.81	3.04E-11	2197
16	In-Plane	0.02995	1.75	14.3	1.71E-11	3047
17	In-Plane	0.02995	1.66	13.55	3.8E-11	1921
Charred						
Sample #	Orientation	Length(m)	Mass C (g)	ρ (lb/ft3)	Ko (m2)	b (Pa)
1	Transverse	0.01996	0.96	13.27	3.39E-11	2381
2	Transverse	0.01996	0.94	13.1	3.49E-11	2639
3	Transverse	0.01996	N/A	13.35	4.66E-11	2275
4	Transverse	0.01996	0.95	13.15	3.33E-11	2844
5	Transverse	0.01996	0.94	13.07	3.75E-11	2365
6	Transverse	0.02995	1.37	13.06	3.86E-11	2482
7	Transverse	0.02995	1.39	13.12	3.74E-11	2551
8	Transverse	0.02995	1.38	12.96	4.25E-11	2424
10	In-Plane	0.01996	0.98	13.55	6.55E-11	1557
11	In-Plane	0.01996	1.03	14.08	6.31E-11	1542
12	In-Plane	0.01996	1.02	14.09	5.67E-11	1781
13	In-Plane	0.01996	1.01	13.82	5.99E-11	1445
14	In-Plane	0.01996	1.01	13.96	3.49E-11	2407
15	In-Plane	0.02995	1.49	13.81	4.91E-11	1876
16	In-Plane	0.02995	1.52	14.3	2.99E-11	2722
17	In-Plane	0.02995	1.46	13.55	6.13E-11	1648